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MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

SEVENTH QUARTERLY TECHNICAL SUMMARY REPORT  
1 April 1963 - 30 June 1963

ARPA Order No. 23-62, Amendment No. 28  
Project Code No. 9100

M.R.I. Project No. 2551-P

For

Director  
Advanced Research Projects Agency  
Washington, D. C.

MRI

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by

Thomas A. Milne

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## PREFACE

This report was prepared for the Advanced Research Projects Agency under ONR Contract No. Nonr-3599(00) monitored by Dr. Ralph Roberts and Mr. Roland Jackel of the Power Branch, ONR. The report describes the application of a high pressure molecular beam sampling system to pure gases, mixtures, and 1 atmosphere flames with additives.

The research staff consists of Dr. Thomas A. Milne, project leader, Dr. Frank T. Greene and Mr. George Vowels. Mr. Gordon E. Gross has been particularly helpful in discussions about the aerodynamics of beam formation.

Approved for:

MIDWEST RESEARCH INSTITUTE



Sheldon L. Levy, Director  
Mathematics and Physics Division

2 August 1963

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### SUMMARY

In our supersonic molecular beam sampling system the previously reported mass separation phenomenon was shown to be independent of temperature from 300 - 2200°K. Large quantities of polymeric species were observed in beams from simple gases at 1 - 7 atmospheres and at room temperature. Evidence is presented that these polymers are formed from supercooled gas in the process of condensing due to the extremely rapid cooling in isentropic expansion to high Mach number beams. The behavior of the anhydrous CO-O<sub>2</sub>, CO-N<sub>2</sub>O, and C<sub>2</sub>N<sub>2</sub>-O<sub>2</sub> flames was studied at several dilutions. The CO-O<sub>2</sub> flame was used in a preliminary study of the dissociation of Cl<sub>2</sub> at 1600 - 2000°K to test the quenching efficiency of the sampling system.

## I. INTRODUCTION

In previous progress reports<sup>1/</sup> we have described experiments aimed at understanding the formation of beams from high pressure sources and some preliminary applications of our aerodynamic molecular beam apparatus to reactive systems, including metal-containing flames. It was felt desirable to study the phenomena encountered in such sampling in some detail since they cannot at present be predicted theoretically.

The study of beam formation so far has led to an appreciation of the problems and behavior to be expected when Knudsen beam experiments are carried out at pressures beyond the molecular flow range. Also the rather surprising and significant "mass separation" effect has been characterized quantitatively to a first approximation, yielding the following proportionality between observed mass-spectrometer ion intensity and partial pressure and molecular weight of species at pressures above 10 - 20 Torr:  $I_{M^+} = kP_M(M.W.)_M$ .

During the past quarter, continued experiments on beam formation from gases at pressures up to 7 atmospheres have led to the observation of the formation of appreciable quantities of astonishingly large polymers of simple gases. This phenomenon has been studied extensively and is reported in the next section along with additional results on mass separation and beam formation. The third section describes our progress toward sampling known equilibria in flames.

## II. SAMPLING OF PERMANENT GASES AND MIXTURES AT HIGH PRESSURES

### A. Beam Behavior - Mass Separation

Additional experiments were carried out testing the dependence of beam intensity on source pressure for simple gases as a function of various first orifice sizes and orifice-skimmer distances with a fixed skimmer (second orifice) size. The results show several anomalies such that at present the dependence of  $I$  on  $P_0$  for a given slit system in an apparatus will have to be empirically determined. However, the beam intensity at one atmosphere is practically constant for flat, thin orifices of from 0.002 in. diameter to 0.009 in. diameter. In experiments with  $CO_2$  at high pressure, the  $CO_2^+$  peak was observed to go through a maximum near 1 atmosphere and then begin to rise again as shown in Fig. 1. A similar tendency was noticed with argon and  $N_2$  indicating that strong beams may be obtained from sources at well beyond 1 atmosphere.

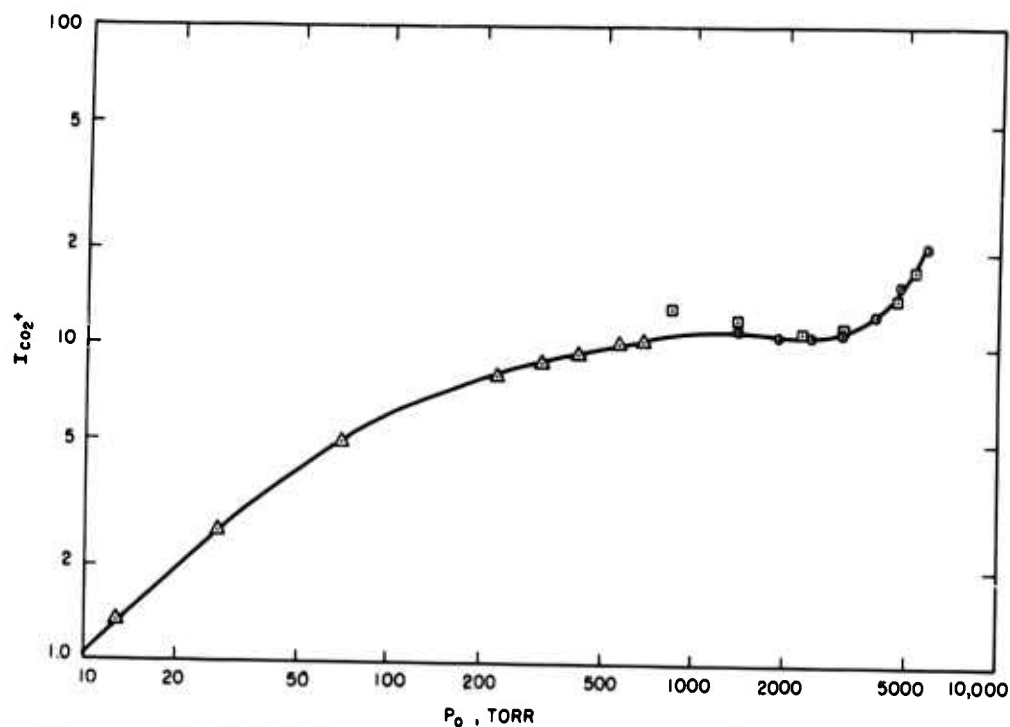


Fig. 1 -  $CO_2$  Beam Intensity vs. Source Pressure.  $T = 300^\circ K$ , 0.002 in. Diameter Orifice, Orifice-Skimmer Distance  $1/4$  in. Intensities in Arbitrary Units.

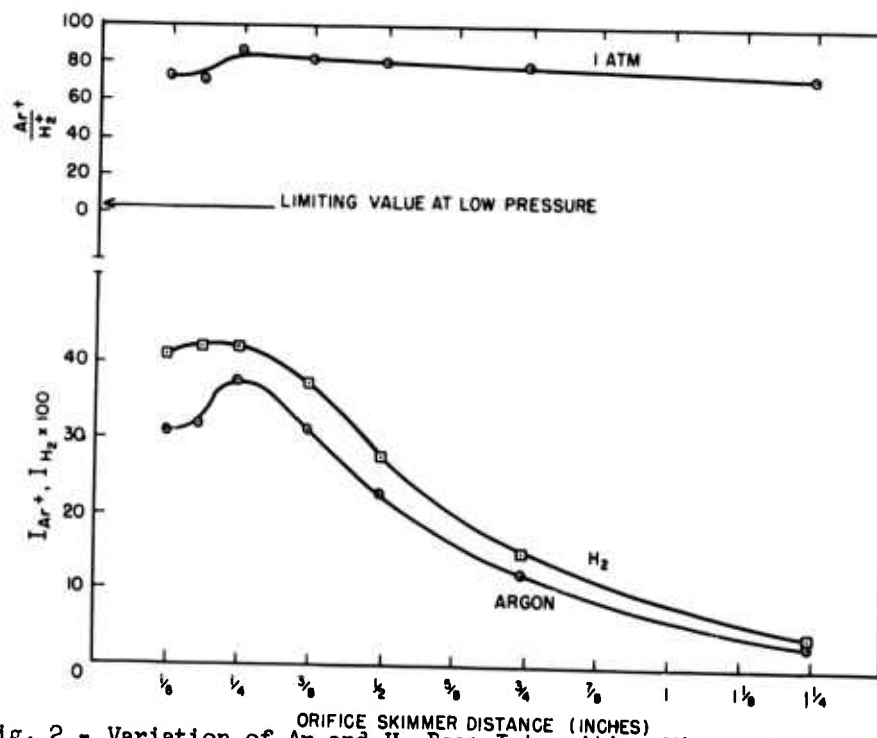


Fig. 2 - Variation of Ar and  $H_2$  Beam Intensities With Orifice-Skimmer Distance for an Equimolar Mixture at 1 Atmosphere,  $300^\circ K$ , and 0.002 in. Diameter Orifice. Intensities in Arbitrary Units.

Additional experiments with gaseous mixtures were carried out. A study of a binary  $H_2$ -argon mixture as a function of orifice-skimmer distance and as a function of source pressure was carried out using a small orifice so that  $P_1$  was maintained at a pressure of a few microns and good beam conditions were maintained. The results are shown in Figs. 2 and 3 and confirm previous generalizations about the lack of dependence of mass separation on orifice-skimmer distance, at least for large distances; and the behavior with source pressure. Of interest in Fig. 3 is the observation that the argon intensity curve has very nearly the same shape as a curve for pure argon, with absolute intensities two to three times less. The  $H_2$  curve on the other hand drops off markedly from the pure  $H_2$  curve at higher pressures. Thus it is more accurate to speak of mass separation as depletion of the lighter component in the beam rather than an enrichment of the heavier component.

The effect of temperature on the mass separation phenomenon was studied under conditions approximating those to be encountered in our flame sampling studies. Thus, about 1 per cent each of the rare gases, He, Ne and Ar were added to a stoichiometric  $CH_4$ -air mixture. The relative intensities were then measured with the gases ignited and unignited, giving a temperature variation of  $300^\circ K$  to about  $2200^\circ K$ .

In three separate runs the absolute and relative intensities of the gases were constant to within 10 per cent with the flame on or off as shown by the data in Table I. In addition the first power molecular weight effect relating observed ion intensities to pressure was confirmed although once again the main solvent gas,  $N_2$ , departed significantly from the rare gas solute behavior.

TABLE I

<u>Average of Three Runs</u>	<u>Ion Intensities</u>			
	<u>He</u>	<u>Ne</u>	<u><math>N_2</math></u>	<u>Ar</u>
Flame off	0.011	0.022		0.40
Flame on	0.010	0.024	19.7	0.37
Normalized Intensity Ratio $\left( \frac{\text{Calculated}}{\text{Actual}} \right)$	on 11.7	2.34		1.0
	off 12.2	2.92	2.44	1.0
$\left( \frac{40}{M.W.} \right)$	10.0	2.0	1.43	1.0

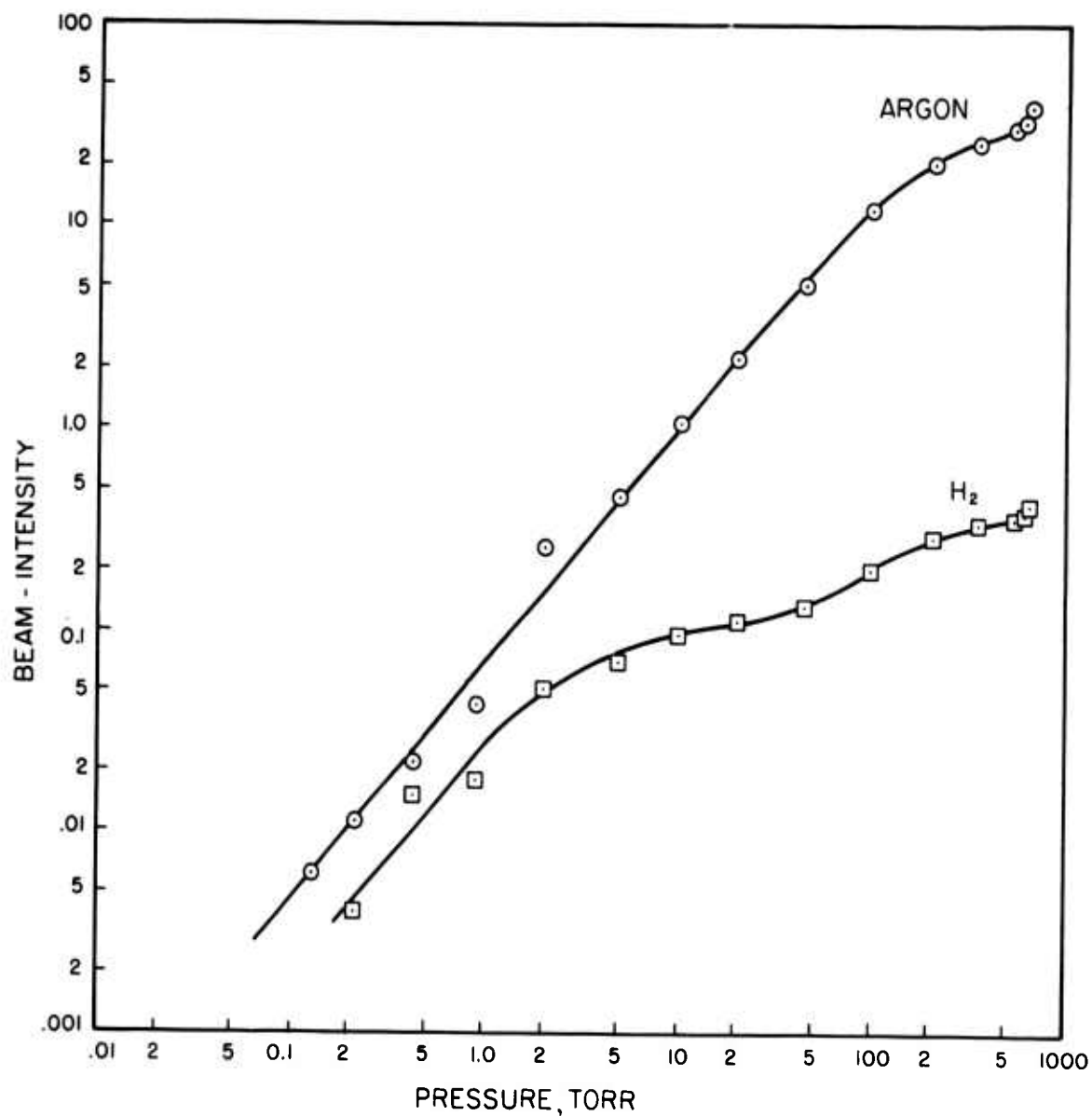


Fig. 3 - Variation of Ar and H<sub>2</sub> Beam Intensities With Source Pressure for an Equimolar Mixture at 300°K and 0.002 in. Diameter Orifice. Intensities in Arbitrary Units.

## B. Formations of Polymers During Sampling

In 1961 two independent reports of the observation of polymeric ions in the mass spectrum of beams formed from high pressure  $\text{CO}_2$  appeared. Bentley<sup>2/</sup> and Henkes<sup>3/</sup> each employed beam systems similar to ours in which one would expect to form a supersonic molecular beam. Bentley, apparently thinking that the very small Joule-Thompson cooling was predominant during beam formation, was at a loss to explain the origin of  $\text{CO}_2$  polymers which could give rise to the observed ions in the mass spectrum. He concluded, tentatively, that they were always present in  $\text{CO}_2$  at the pressure sampled (3,800 Torr). Subsequently, Turnbull,<sup>4/</sup> with the same apparatus, continued the study of these polymers in  $\text{CO}_2$  and several other gases and postulated that they might be formed in a shock wave between the first and second orifice.

Henkes,<sup>3/</sup> with the background of work dating back to 1956 or earlier with E. W. Becker's<sup>5/</sup> group, also observed these polymeric ions in the spectrum from  $\text{CO}_2$  and attributed their formation to a partial condensation of the gas during the extreme and rapid adiabatic cooling occurring in the initial expansion.

The existence and conditions of formation of such polymers in beams from high pressure gases was of considerable interest to us in our present work because of: (1) the insight it might give as to the nature of the expansion of the gas to a molecular beam; (2) its pertinence to the kinetics of freezing out equilibria in reactive systems; (3) the possibility of mistaking these species, generated in the process of sampling, for those present in equilibrium in the system being sampled; and (4) the unusual molecules produced, their stability and ionization behavior, and the kinetics of their formation.

Table II lists the ionic species observed in beams from various gases under the stated conditions using our molecular beam sampling system with either an 0.002 in. diameter flat orifice or an 0.009 in. diameter conical orifice, with all other parameters as described in earlier reports. We confirm the observations of Bentley and Henkes for  $\text{CO}_2$ , finding even larger abundances and higher polymers. Our quantitative detection of  $\text{CO}_2$  polymers stopped at  $(\text{CO}_2)_{15}$  only because the standard gate delay on the Bendix time-of-flight mass spectrometer was limiting. Figure 4 shows a plot of intensity of ionic species vs. number of polymeric units, with Bentley's data for comparison. Also noteworthy from Table II is the extent of polymerization observed for argon (plotted in Fig. 4). The  $\text{H}_2\text{O}$  and  $\text{NH}_3$  results show similarity, particularly in the near absence of parent polymer ions and the predominance of ions representing the parent polymer less an OH or  $\text{NH}_2$  group.

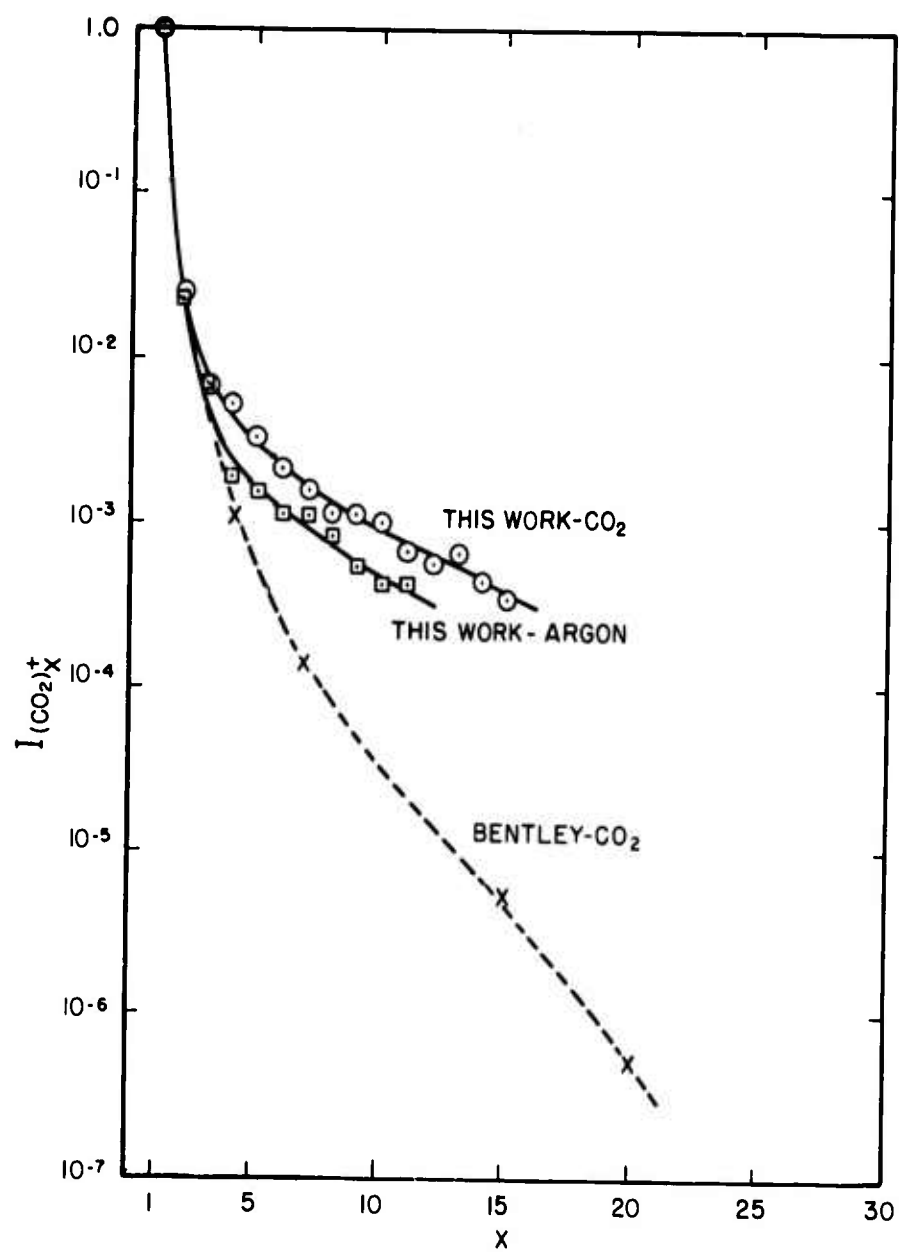


Fig. 4 - Relative Polymeric Ion Intensities Observed for CO<sub>2</sub> and Argon at 5 Atmospheres and 300°K, 0.002 in. Diameter Orifice

TABLE II

SPECIES OBSERVED IN BEAMS FROM VARIOUS GASES

<u>Gas</u>	<u>Conditions</u> (Room Temp. Except Where Noted)	<u>Ionic Species Observed</u>
Ne	1-3 atm.	20 <sup>+</sup> , 40 <sup>+</sup>
Ar	1-7 atm.	40 <sup>+</sup> , 80 <sup>+</sup> , .... 440 <sup>+</sup> .... higher
H <sub>2</sub>	1-5 atm.	2 <sup>+</sup>
N <sub>2</sub>	1-5 atm.	28 <sup>+</sup> , 56 <sup>+</sup>
O <sub>2</sub>	1-5 atm.	32 <sup>+</sup> , 64 <sup>+</sup>
H <sub>2</sub> O	1 atm. Steam and Humid Air }	18 <sup>+</sup> , 19 <sup>+</sup> , 37 <sup>+</sup> , 55 <sup>+</sup> , 73 <sup>+</sup>
D <sub>2</sub> O	Satd. Air, 1 atm.	20 <sup>+</sup> , 22 <sup>+</sup> , 42 <sup>+</sup> , 62 <sup>+</sup> , 82 <sup>+</sup>
N <sub>2</sub> O	1 atm.	44 <sup>+</sup> , 88 <sup>+</sup> .... higher
CO <sub>2</sub>	1-5 atm.	44 <sup>+</sup> , 88 <sup>+</sup> , .... 660 <sup>+</sup> .... to >1200 <sup>+</sup>
NH <sub>3</sub>	1-2 atm.	17 <sup>+</sup> , 34 <sup>+</sup> , 35 <sup>+</sup> , 52 <sup>+</sup> , 69 <sup>+</sup> , 86 <sup>+</sup> , 103 <sup>+</sup>
CH <sub>4</sub>	1-5 atm.	16 <sup>+</sup> , 32 <sup>+</sup> (?)
CCl <sub>4</sub>	Satd. Argon, 1 atm.	No polymers visible
n-Butane	1-3 atm.	" " "

A convincing explanation of the origin of these species emerges from a study of the ions listed in Table II, Figs. 5 and 6 which show the behavior of argon monomer and dimer as source pressure and orifice-skimmer distance are varied, and a consideration of the processes which occur in beam formation from high pressure sources. Under the conditions present in the first stage of our sampling system the gas expands isentropically and adiabatically, forming a supersonic molecular beam of quite high Mach number. According to the measurements of Fenn and Deckers<sup>6/</sup> which agree with calculations to Mach numbers around 8 - 10, beam Mach numbers of 10 or more are very likely in our particular sampler. The beam achieves these Mach numbers at the expense of its own internal and random translational energy, so that a strong cooling of even an ideal gas occurs. In the ideal case of isentropic expansion of a gas from rest at a temperature  $T_0$  to a Mach number of  $M$  the final temperature of the gas is given by:

$$T/T_0 = \left( 1 + \frac{\gamma-1}{2} M^2 \right)^{-1}$$

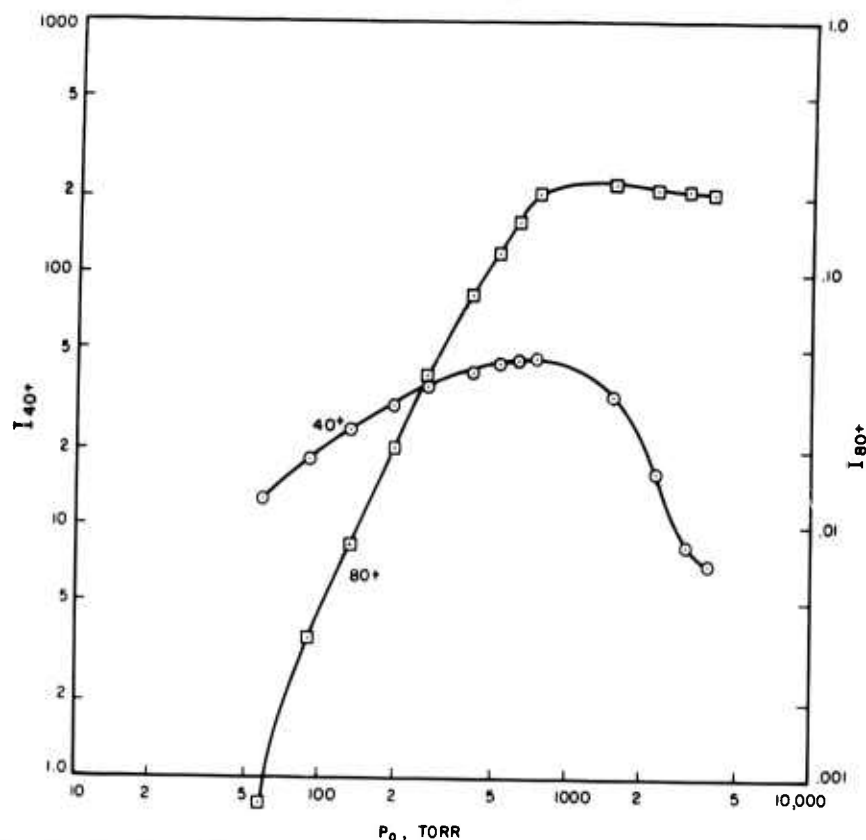


Fig. 5 - Variation of Argon Monomer and Dimer Beam Intensity vs. Source Pressure.  $T = 300^\circ\text{K}$ , 0.002 in. Diameter Orifice, Orifice-Skimmer Distance  $1/8$  in. Intensities in Arbitrary Units.

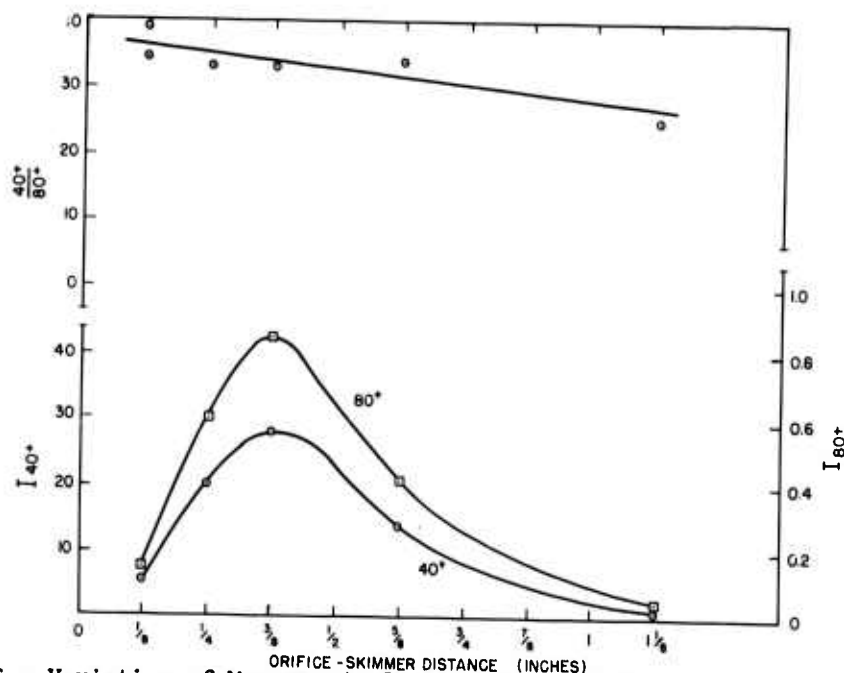


Fig. 6 - Variation of Monomer-to-Dimer Ratio in Pure Argon with Orifice-Skimmer Distance. 5 Atmospheres,  $300^\circ\text{K}$  and 0.002 in. Diameter Orifice. Intensities in Arbitrary Units.

The cooling is seen to be a function of  $M$  and  $\gamma$ , the ratio of specific heats, of the gas. For beams of Mach 10 and 5, from various gases at room temperature, the final temperature of the beam molecules is given in Table III. As can be seen the cooling is extreme leaving the beam molecules in very low energy states if equilibration is maintained. Thus, depending on the starting conditions of the gas, such cooling may cause the gas to become supersaturated with respect to solid or liquid during expansion. Since we ultimately expand the gas into the collisionless molecular flow regime, the kinetics of condensation or polymerization come into play and in practice we catch the gas in an intermediate stage of condensation.

This phenomenon is well known to aerodynamicists in supersonic wind tunnel studies, the condensation there often proceeding to liquid or solid and giving rise to so-called condensation shocks. Becker and co-workers<sup>5</sup> postulated the existence of such "condensed molecular beams," based on indirect evidence, several years ago, but only in the recent work mentioned above are the stepwise species observed in a mass spectrometer.

With this phenomenon then, we are really dealing with one aspect of the broad question of the extent to which an equilibrium can be frozen during sampling. The fact that such species are being formed adds one more bit of evidence that we are expanding the gas to rather high Mach numbers and the fact that they survive into the final beam in significant proportions implies that if the gas is going through a shock wave in front of the skimmer, the shock is too diffuse to have much effect on species.

TABLE III

EXTENT OF COOLING IN SUPERSONIC BEAMS

$T_0 = 300^\circ\text{K}$ Ratio of Specific Heats $\gamma$	Final Beam Mach No. $M$	Final Beam Temp. $T, ^\circ\text{K}$
5/3 (Monatomic)	10	8.8
7/5 (Actual Diatomic)	10	14.3
9/7	10	19.6
5/3	5	32.0
7/5	5	50.0
9/7	5	65.6

The extent of polymerization observed can be explained qualitatively by considering how far the gas is from saturation initially, the  $\gamma$  of the beam gas, the intermolecular forces in the gas. Thus, referring to Table II, more polymers might be expected in Ar than in  $N_2$  and  $O_2$  since the cooling would be greater in Ar. Likewise, the extent of polymerization in  $CO_2$  and  $H_2O$  is perhaps not as great as expected, in view of the closeness to saturation of the starting gas and the large intermolecular forces present, due to the lower  $\gamma$  for these species and hence decreased cooling rates.

To confirm these general relations, a number of experiments were carried out with several gases. It was observed, for instance, that a higher percentage of water polymers was present in room temperature air, saturated with water (about 1 per cent  $H_2O$ ), than in pure steam at  $100^\circ C$ . Apparently the diatomic carrier (air) cools the  $H_2O$  more rapidly, overcoming the less frequent collisions in the 1 per cent dilution and creating more polymerization. This same effect is illustrated for the  $CO_2$  monomer and dimer in Fig. 7. Here the ratio of  $44^+/88^+$  is plotted versus dilution of the  $CO_2$  by various gases. It is seen that the extent of polymerization increases for some time with added  $N_2$  and with argon increases to the surprising dilution of about 2.5 per cent  $CO_2$ . At this point the dimer intensity is about one-third that of the monomer. The reverse effect is shown in Fig. 8 in which the monomer-to-dimer ratio for argon is plotted versus addition of various gases. The addition of very small amounts of  $CO_2$  or  $D_2O$  apparently profoundly affects the expansion and severely reduces the dimer formation. The argon monomer intensity is also affected markedly by addition of  $CO_2$ , 5 per cent  $CO_2$  reducing the  $40^+$  signal to almost one-half of its original value. The mono and diatomic gases increase the  $40^+/80^+$  ratio but much less rapidly.

Precooling or preheating the gases likewise affects the extent of polymerization as we have observed with cooled  $CO_2$ ,  $N_2$ , and argon and  $H_2O$  in heated air. Henke's<sup>7/</sup> results with  $H_2$  sampled at liquid  $H_2$  temperatures are quite startling, indicating polymers to over  $(H_2)_{550}$  with the higher polymers predominating over the lower ones. It should be mentioned at this point that some caution must be used in deducing true high polymer concentrations from observed ion intensities, apart from problems of fragmentation. Thus, if our observed mass separation effect held for  $(Ar)_{10}$  and if the relative ionization cross section were proportional to the number of Ar atoms in the molecule as has often been assumed in simpler cases, then the actual ion intensities

$\frac{(Ar)_{10}^+}{Ar^+}$  might be 100 times the ratio of neutrals initially formed. Of course, it is not clear just how the mass separation effect is tied in with the expansion and beam formation and hence how it may be coupled with polymer formation.

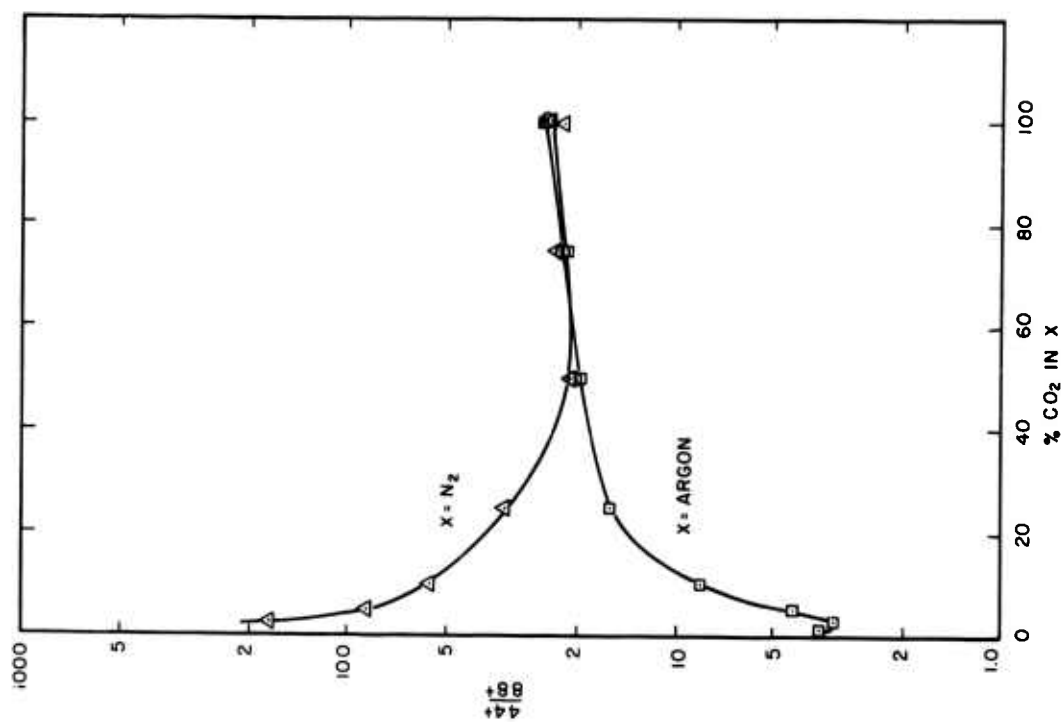


Fig. 7 - Effect of Additives on the Monomer-Dimer Ratio in CO<sub>2</sub> at 1 Atmosphere and 300°K

○ and △ are for N<sub>2</sub>.

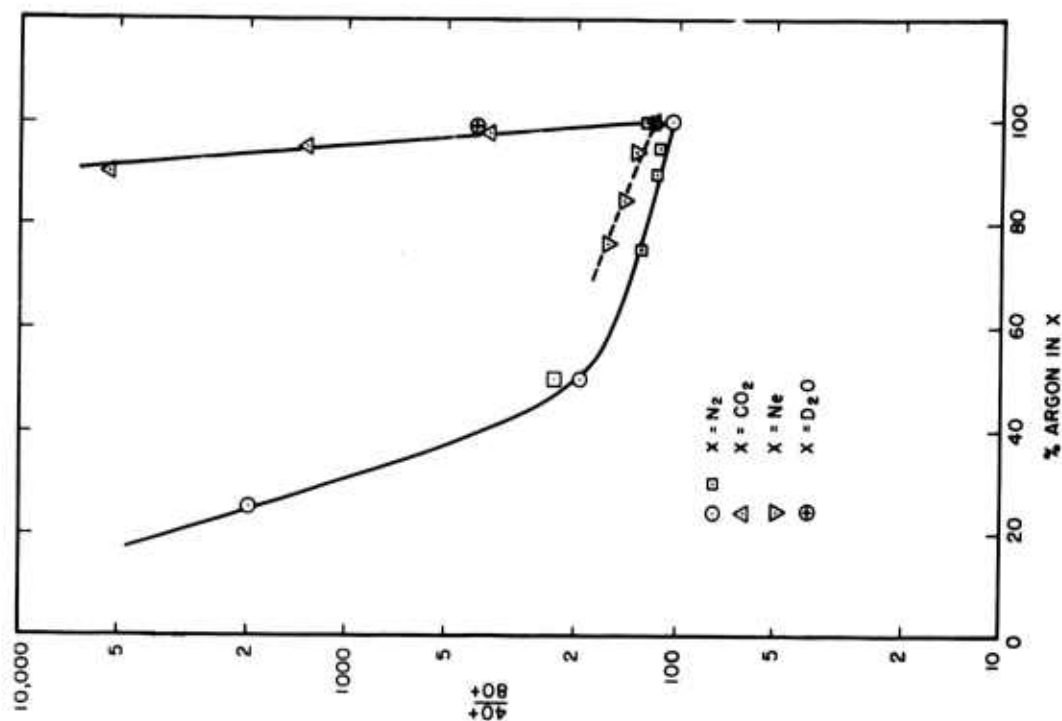


Fig. 8 - Effect of Additives on the Monomer-Dimer Ratio in Argon at 1 Atmosphere and 300°K.

The easy production of these unusual polymer species in rather high concentration leads to interest in the nature of the molecules and their behavior. There appears to be no necessity to invoke any bonding forces in these polymers other than those forces responsible for holding the liquid together or giving departures from ideal gas behavior -- the simple van der Waals forces. Thus, one can consider the molecule  $(Ar)_2$  in terms of one of the popular equations for describing gaseous imperfections, say the Lennard - Jones 6-12 potential. This potential, with typical constants determined from PVT data, predicts a stable molecule with  $r_e$  about 4A and  $D_e$  about 0.01 ev. The equilibrium concentration of such a molecule in argon gas will never be very great, at pressures less than a few atmospheres, at any temperature. However, in the expanding gas at high Mach numbers, the collisional translation energy is reduced to such a low value that  $Ar_2$  can form as a step in the condensation process and the continued expansion to molecular flow then preserves it in the beam in the high concentrations observed.

Such weakly bound molecules will not survive collision with walls or gas molecules. This is confirmed by the virtual 100 per cent shutter dependence observed for the polymers, but not for the monomer. The fact that these weakly bound clusters apparently form appreciable amounts of parent ions on electron impact with 50 ev electrons is also interesting.

The conditions of formation and behavior of these polymers will in many cases allow them to be distinguished from species actually in equilibrium in the gas being sampled. However, their possible presence must make one cautious in studying minor species in unknown systems or in studies of equilibrium polymerization in gases like  $H_2O$ ,  $HF$ , acetic acid,  $NO_2$ , sulfur vapor, etc., at pressures greater than 10 - 100 Torr. It might be thought that in flame studies, the high temperature of the flame combustion product gases would preclude the formation of polymers because the starting gases are greatly superheated with respect to condensation. This is true as far as the products like  $H_2O$ ,  $CO_2$ ,  $CO$ , and  $N_2$  are concerned, but when one is studying additives in flames which form products of low volatility ( $HBO_2$ ,  $AlO$ ,  $LiOH$ , etc.) then one again has the condition for polymer formation, namely nearness to saturating at the temperature of the source gas. Our future experiments will assess the seriousness of such complications in studying high temperature equilibria.

### III. FLAME STUDIES

Our work on the sampling of flames during the past quarter has included temperature measurements on flames of immediate interest, the study of anhydrous flames, and a continuation of the measurement of known equilibria to test the quenching efficiency of the sampling system.

#### A. Flame Temperature Measurements

Present flame temperature measurements are being made using the sodium line reversal technique. The apparatus is similar to the one described by Gaydon.<sup>8/</sup> A General Electric Type 18A/T10/6 Spectrograph lamp is focused in the center of the flame being studied. The flame and the lamp are then focused on the slit of a Bausch and Lomb Model ED 7929 constant deviation spectroscope. The temperature of the lamp is measured with a Leeds and Northrop optical pyrometer. Sodium is introduced by means of a NaCl evaporator placed in the oxygen line. The sodium chloride vapor condenses as a very fine dust as it is swept from the evaporator, and is carried into the flame in sufficient quantity.

The line reversal apparatus was used to measure temperatures in the several flames noted below. Reproducibility is well with  $\pm 20^\circ$  for the hotter flames. This is more than adequate for present purposes.

#### B. Anhydrous Flames

The anhydrous flames which appear to be most suitable for thermochemical studies are the cyanogen-oxygen, carbon monoxide-oxygen, and carbon monoxide-nitrous oxide. The burning characteristics of these three flames were studied, particularly with respect to the dilution which is necessary to obtain temperatures in the range  $1500^\circ - 2000^\circ\text{C}$ .

The cyanogen-oxygen flame was found to give a relatively convenient, stable flame with conventional burners even when diluted with sufficient nitrogen to obtain an adiabatic flame temperature of the order of  $1800^\circ\text{C}$ . Unfortunately, cyanogen is no longer being manufactured and has a limited "shelf" life. Consequently, it would seem advisable to use other flames wherever possible.

The carbon monoxide-oxygen flame was studied extensively. Although no hydrogen or hydrogen-containing species could be detected by mass spectrometric analysis, a stable stoichiometric flame was readily obtained. This flame was diluted with Ar,  $\text{N}_2$ , and  $\text{O}_2$ . For all three gases the maximum dilution possible was about 4 moles per mole of CO. For oxygen this gives an adiabatic flame temperature of about  $1700^\circ\text{C}$ . At higher dilutions the flame speed dropped very sharply to below the useful range.

The carbon monoxide-nitrous oxide flame was also studied. It was found to have no practical advantage over the carbon monoxide-oxygen flame and to be thermochemically disadvantageous when cool flames are required.

### C. Flame Sampling

Preliminary experiments have been designed to test the operation of the sampling system by actually sampling high temperature equilibrium in flames. The Cl-HCl and Cl-Cl<sub>2</sub> equilibria were chosen for study because they have well known thermochemistry, can be introduced as gases, and introduce a minimum of mechanical problems such as orifice stability and plugging.

Several difficulties arose in the study of the chlorine equilibria. Chlorine inhibits most combustion processes and large quantities change the physical characteristics of the flame. Furthermore, the additional chlorine repressed the dissociation of NaCl and prevented temperature measurements by sodium line reversal. It was, therefore, necessary to add sufficiently small quantities of chlorine so that there was no visible perturbation of the flame's reaction zone and make measurements assuming that temperatures through the flame were unchanged.

Chlorine was introduced into a lean CO-O<sub>2</sub> flame (2.1 moles O<sub>2</sub>/mole CO) and sampled in several portions of the burnt gas region of the flame. The results are given in Table IV. The agreement of the observed Cl/Cl<sub>2</sub> ratio with those calculated only to within an order of magnitude may indicate poor quenching. However, since the flame was visibly perturbed by the orifice plate, the temperatures were quite uncertain. Future temperature measurements will be made with the flame impinging on the orifice.

Anhydrous HCl was introduced into a methane-oxygen flame, and the Cl-HCl ratio measured. The results are not reported, as flame temperatures have not yet been directly measured.

TABLE IV

<u>Temperature</u> <u>(°K)</u>	<u>Cl/Cl<sub>2</sub></u> <u>Calculated</u>	<u>35<sup>+</sup>/70<sup>+</sup></u> <u>Observed</u>	<u>Cl/Cl<sub>2</sub></u> <u>Corrected*</u>
1694	5	0.87	2.7
1897	26	1.25	3.6
1968	48	2.13	6.0

\* The observed ion ratios were corrected for fragmentation, ionization cross section, and mass separation.

#### IV. FUTURE WORK

It appears now that the major difficulties encountered in beam formation from 1 atmosphere sources have been characterized and their effect on sampling determined to a first approximation. Thus, the effects of mass separation and polymerization during beam formation can be allowed for and, as future flame thermochemical studies demand, put on a more precise quantitative basis.

Our future work will be more heavily oriented toward actual sampling of flames with additives and problems directly related to production of the appropriate flames, their temperatures and interaction with the sampling probe. Most of the effort will be expended on demonstrating the ability to quantitatively sample known equilibria in flames. Other systems will be examined, however, where new or poorly known species may be present, and where qualitative or semiquantitative studies would have thermochemical value. Additives such as B, Al, Na, Mg, Fe, and Ni will be explored in various flame environments.

Modifications in the beam system will be made to provide more versatility in the use of burners and orifices, and to permit rapid replacement of damaged or plugged orifices and skimmers. Attempts will be made to increase the useful sensitivity of the mass spectrometer in regions of normally high background by cleaning up the sampling system or by using a pulsed beam and phase sensitive detectors, or both.

Finally, continued attention will be given to the process of beam formation, and, in particular, how the expansion history of the beam gas, when coupled with kinetics of pertinent reactions, may be used to estimate the extent of polymer formation and quenching of reactive equilibria in a supersonic molecular beam.

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